# PATENT SPECIFICATION

357,135

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PROVISIONAL SPECIFICATION.

## Improvements in the Catalytic Manufacture and Production of Carbon Black.

I, JAMES YATE JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organized under the Laws of Germany) to be as follows:—

In the processes hitherto proposed for the manufacture and production of carbon black by the thermal decomposition of gaseous or vaporous hydrocarbons, for example of unsaturated hydrocarbons or of carbon monoxide in the presence of catalysts, the activity of the catalyst frequently subsides after a short time and the gases are only incompletely decomposed. This phenomenon is due, especially when the catalyst is at rest in the reaction vessel, to the fact that the catalyst does not come into contact intimate enough with the gases to be decomposed. Even when working with pulverulent catalysts or with rotary tube furnaces or rotary drums in which the catalyst is kept in motion, this objection still occurs. Furthermore, especially when employing stationary catalysts, the carbon black is frequently deposited in more or less thick layers on the walls of the reaction vessel and thus hinders the uniform heating of the gases passed therethrough. Moreover local overheating may readily take place with consequent agglomeration of the carbon black and this very unfavourably influences the quality of the latter.

My foreign correspondents have now found that an almost complete decomposition of the gases to give a carbon black having a high degree of dispersion and a uniform character is effected by carrying out the decomposition in a vessel which is provided with means whereby the catalyst is moved through the free space of the vessel. The favourable effect of working in this manner is especially noticeable when the catalyst is employed in a finely divided form, as for example as a powder.

In order to carry out the process according to the present invention, conveyor worms, bucket wheels, scrapers or shaking sieves or spreaders are arranged for example in the decomposition chamber. By their rotation, vibration or the like these devices ensure that the catalyst remains for a sufficiently long period of time in the free space of the decomposition chamber and moreover they prevent the carbon black settling on the walls of the vessel. In vertical decomposition vessels it is often sufficient to arrange inclined surfaces opposite to each other, down which the catalyst slides and falls from one to the other. When employing horizontal or inclined decomposition vessels, the catalyst may be whirled in the full space of the said vessels by devices such as blade or bucket wheels, scrapers or the like, and thus brought into intimate contact with the gas. A vessel which is very suitable in many cases is obtained by providing the inner wall of a horizontal or inclined tube which is rotating about its longitudinal axis with longitudinal ribs, grooves or undulating projections. These raise the catalyst or the mixture consisting of the catalyst and carbon black to a certain angle of inclination and then allow it to fall down through the free space through which the gas to be decomposed is flowing. The mixture may be led repeatedly through the decomposition chamber until the catalyst is so much diluted by carbon black that it is no longer capable of decomposing the gas sufficiently. The catalyst may also be blown into the free space of the reaction vessel by means of gases, which may if desired be extraneous or may participate in the reaction. It may also be advantageous to maintain the catalyst in suspension in the reaction chamber.

The inner surfaces of the wall of the decomposition vessel and the devices provided thereon are preferably constructed of a material which promotes the decomposition of the carbonaceous gases, as for example copper, manganese-copper, zinc and the like.

As catalysts may be employed all of those catalysts facilitating the formation of carbon black which are available in a powdery form, especially those contain-

[Price 1/-].

ing the elements of the iron group and to which small amounts for example from 0.1 to 10 per cent. of an activator have been added. As activators may be mentioned the oxides, hydroxides, carbonates, nitrites, nitrates, cyanides, complex cyanides, chromates and other salts of the alkali metals, alkaline earth metals, magnesium, zinc, aluminium, tin, cadmium, lead and bismuth.

By reason of the intimate mixing of the gas to be decomposed with the catalyst, an excellent yield per unit of time and space is obtained according to the present invention, especially when the decomposition vessel is so constructed that carbon black may be periodically or continually removed and a corresponding amount of catalyst supplied. The formation of crusts and lumps is prevented by the continual movement of the carbon black formed, and the carbon black is obtained as a loose powder having an extremely high degree of dispersion so that it is eminently suitable as a filler for the rubber industry and also for other purposes for which the said property is important.

The preparation of carbon black according to the present invention may also be carried out at increased pressure and in the presence of additional gases or vapours. The gases or vapours may be introduced at different places into the vessel and may be introduced at several places simultaneously.

The nature of the invention will be further described with reference to the accompanying drawing which illustrates apparatus especially suitable for carrying out the process according to the present invention. Figure 1 represents a longitudinal section of an apparatus the essential part of which is a horizontal tube capable of being rotated about its longitudinal axis. Figure 2 shews a cross-section of the said tube. Figure 3 represents a vertical section of an apparatus fitted with a vertical decomposition vessel. Figures 1 and 2 have reference to Example 1 Figure 3 to Example 2 which Examples illustrate the nature of this invention, but the invention is not restricted either to these Examples or to the specific kind and arrangement of the apparatus shewn in the accompanying drawing.

EXAMPLE 1.

5 grams of fine cobalt powder obtained by the decomposition of cobalt carbonyl are introduced into the horizontal vessel A, shewn in Figure 1. This vessel is 60 centimetres long and 20 centimetres in diameter and is caused to rotate about its longitudinal axis and its inner wall consists of manganese-copper and is provided with longitudinal ribs B shewn in Figure 2, which ribs also consist of manganese-copper. After hydrogen has been led through the vessel for 3 hours, the vessel being kept at 350° Centigrade by means of the electrical heating jacket C, a gas mixture obtained by the high temperature carbonisation of brown coal and carefully purified from sulphurous impurities (composition: 13.5 per cent. of carbon di oxide, 5.7 per cent. of carbon monoxide, 17.5 per cent. of methane, 3.1 per cent. of ethane, 1.8 per cent. of propane, 28.9 per cent. of ethylene, 12.8 per cent. of propylene, 6.4 per cent. of butylene and 10.3 per cent. of nitrogen) is led through the pipe D into the vessel A with a velocity of flow of 70 litres per hour, the vessel being kept at from about 370° to 380° Centigrade. The mixture of the carbon black thus formed and the catalyst rotates with the vessel through about 120° by reason of the longitudinal ribs B, falls through the free gas space by reason of its weight and is then raised again by subsequent ribs. The gas leaving the vessel through the outlet E contains about 70 per cent. of hydrogen. After about 8 hours the vessel contains 500 grams of an extremely voluminous soft deep brown-black carbon black having an entirely homogeneous nature which is eminently suitable for direct employment as a filler for the production of rubber-like masses from natural rubber or polymerisation products of butadiene. Part of the carbon black is collected in the vessel F and may be removed at G.

EXAMPLE 2.

A vertical decomposition vessel N shewn in Figure 3, 1 metre in length and 15 centimetres in diameter in which is situated a gas-tight rotating axle K provided with sloping surfaces S and funnels M of galvanised sheet iron arranged alternately one above the other in the form of a screen and also provided with galvanised scrapers O, of which only one is shewn in the Figure, is heated by means of the electrical heating jacket R so that the internal temperature is from 380° to 400° Centigrade, and 200 litres of carbon monoxide per hour are led in at F. At the same time a finely powdered catalyst consisting of a mixture of about 80 per cent. of cobalt, 10 per cent. of nickel, 7 per cent. of zinc, 2.5 per cent. of calcium oxide and 0.5 per cent. of potash, which has been previously subjected to a reducing treatment with hydrogen, is introduced at the top by means of a conveyor worm P. The carbon monoxide is practically completely decomposed into carbon dioxide which is withdrawn at the outlet J and carbon black. The carbon black

falls into a vessel arranged at the lower end of the decomposition vessel in the form of a loose powder and may be periodically or continuously withdrawn at H. The catalyst intermixed therewith may be removed by stirring with dilute nitric acid warmed to 50° Centigrade. The resulting carbon black has an extremely high degree of dispersion.

Dated this 13th day of June, 1930.

J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C. 2,
Agents.

COMPLETE SPECIFICATION

## Improvements in the Catalytic Manufacture and Production of Carbon Black.

I, JAMES YATE JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organized under the Laws of Germany) and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to improvements in the manufacture and production of carbon black by thermal decomposition with catalysts of gaseous or vaporous carbon compounds, such as carbon monoxide or unsaturated hydrocarbons in the gaseous phase.

In the processes hitherto proposed for the manufacture and production of carbon black by the thermal decomposition of gaseous or vaporous hydrocarbons, for example of unsaturated hydrocarbons or of carbon monoxide in the presence of catalysts, the activity of the catalyst frequently subsides after a short time and the gases are only incompletely decomposed. This phenomenon is due, especially when the catalyst is at rest in the reaction vessel, to the fact that the catalyst does not come into contact intimate enough with the gases to be decomposed. Even when working with pulverulent catalysts or with rotary tube furnaces or rotary drums in which the catalyst is kept in motion, this objection still occurs. Furthermore, especially when employing stationary catalysts, the carbon black is frequently deposited in more or less thick layers on the walls of the reaction vessel and thus hinders the uniform heating of the gases passed therethrough. Moreover local overheating may readily take place with consequent agglomeration of the carbon black and this very unfavourably influences the quality of the latter.

My foreign correspondents have now found that an excellent carbon black is obtained in an advantageous manner by causing the catalyst to fall through the gases or vapours to be decomposed, and interrupting the state of fall repeatedly. The favourable effect of working in this manner is especially noticeable when the catalyst is employed in a finely divided form, as for example as a powder.

Among the means suitable to cause the catalyst to fall through the reaction space and to interrupt the fall, may be mentioned conveyor worms, bucket wheels, scrapers, shaking sieves or spreaders arranged in the decomposition chamber. By their rotation, vibration or the like, these devices ensure that the catalyst falls for a sufficiently long period of time through the free space of the decomposition chamber and moreover they prevent the carbon black settling on the walls of the vessel. In vertical decomposition vessels it is often sufficient to arrange inclined surfaces opposite to each other, down which the catalyst slides and falls from one to the other. When employing horizontal or inclined decomposition vessels, the catalyst may be whirled in the full space of the said vessels by devices, such as blade or bucket wheels, scrapers or the like, and thus brought into intimate contact with the gas. A vessel which is very suitable in many cases is obtained by providing the inner wall of a horizontal or inclined tube which is rotating about its longitudinal axis with longitudinal ribs, grooves or undulating projections. These raise the catalyst or the mixture consisting of the catalyst and carbon black to a certain angle of inclination and then allow it to fall down through the free space through which the gas to be decomposed is flowing. The mixture may be led repeatedly through the decomposition chamber until the catalyst is so much diluted by carbon black that it is no longer capable of decomposing the gas sufficiently.

The inner surface of the wall of the

decomposition vessel and the devices provided thereon are preferably constructed of a material which promotes the decomposition of the carbonaceous gases, as for example copper, manganese-copper, zinc and the like.

It is often advantageous to preheat the gases in any suitable manner.

As the initial materials for the production of carbon black may be mentioned, for example, carbon monoxide or unsaturated hydrocarbons, and especially olefines, such as ethylene, propylene or butylene, or gases containing the same, such as oil gas, to which other gases or vapours such as water vapour, carbon dioxide and in the case of unsaturated hydrocarbons also carbon monoxide, hydrogen, nitrogen, methane and the like may be added. Small amounts of air may also be added while avoiding the limits of explosion.

As examples of catalysts may be mentioned all of those catalysts facilitating the formation of carbon black, which are available in a powdery form, especially those containing the elements of the iron group as for example those containing cobalt, and to which usually small amounts of for example from 0.1 to 10 per cent. of an activator have preferably been added. As activators may be mentioned the oxides, hydroxides, carbonates, nitrites, nitrates, cyanides, complex cyanides, silicates, chromates, phosphates, and other salts of the alkali metals, alkaline earth metals, or of magnesium, zinc, aluminium, tin, cadmium, lead, bismuth, vanadium, uranium and chromium, or of other metals forming oxides not reducible to the metal with hydrogen at temperatures below 600° Centigrade. Examples of catalysts advantageously employed in the reaction are further those catalysts containing metals or oxides of metals of the iron group which are obtained by heating salts or other compounds or mixtures containing the same which may easily be decomposed at high temperatures, as for example nitrates, nitrites, chlorates, perchlorates and cyanides of iron, nickel or cobalt. Metals obtained by decomposition of the corresponding carbonyl compounds are also very suitable as constituents of the catalyst. Moreover salts of the alkali metals, alkaline earth metals, or of magnesium, zinc, aluminium, tin, cadmium, lead, bismuth, vanadium, uranium, or chromium, stable to high temperatures, such as silicates, phosphates, tungstates and borates, may be employed as catalysts together with the salts easily decomposable by the action of heat. Especially suitable for the production of carbon black from hydrocarbons are the catalysts consisting of three or more different kinds of substances, as for example those which consist of the catalytically acting metal mixed with zinc oxide, calcium oxide or similar oxides and in addition thereto with activators, especially salts of alkali metals.

Although as a general rule atmospheric pressure is employed, the preparation of carbon black according to the present invention may also be carried out at increased pressure and/or in the presence of additional gases or vapours. The employment of increased pressure as for example pressures of 20, 50, 100 or 200 atmospheres, has the great advantage that the reaction is accelerated and that a smaller reaction space is required than with smaller pressures. Pressures of less than atmospheric, as for example a pressure of 0.5 atmosphere, may also be employed, this having the advantage that it is particularly easy to avoid the reaction proceeding too suddenly. This latter effect may also be attained by the introduction of additional gases or vapours. The gases or vapours may be introduced at different places into the vessel or may be introduced at several places simultaneously.

Temperatures suitable for the process according to the present invention range from about 300° to 500° Centigrade. The best results are obtained at temperatures of from about 370° to 380° Centigrade, the optimum temperature being dependent to a certain extent on the kind of catalyst and the pressure employed.

The catalysts employed according to the present invention preferably have a grain size with a mean diameter ranging below 0.1 millimetre and advantageously between 0.01 and 0.0001 millimetre.

The separation of the mixture of the carbon black formed in the process with the catalyst from the gases arising from the reaction may be effected by mechanical means. Electrical dust separators may also be employed.

The separation of the carbon black from the catalyst in such cases where it is obtained mixed with catalysts may be effected in any suitable manner, for example by flotation with a suitable fluid medium, for example, water or oil, or a gas current of suitable velocity. If the catalyst has magnetic properties, the carbon black formed can be separated therefrom by means of a magnet. The catalyst may also be reduced and then dissolved in acids.

By the process according to the present invention injurious local overheating is avoided because a uniform distribution

of the heat of reaction throughout the whole decomposition chamber is effected.

By reason of the intimate mixing of the gas to be decomposed with the catalyst, an excellent yield per unit of time and space is obtained according to the present invention, especially when the decomposition vessel is so constructed that carbon black may be periodically or continually removed and a corresponding amount of catalyst supplied. An almost complete decomposition of the gases is often attained. The formation of crusts and lumps is prevented owing to the continual movement of the carbon black formed, and the carbon black is obtained as a loose powder having a very uniform and an extremely high degree of dispersion, so that it is eminently suitable as a filler for the rubber industry and also for other purposes for which the said property is important. Furthermore, the activity of the catalyst is sustained for a very long time. The invention has the further advantage that the deposition of considerable layers of carbon black on the walls of the reaction vessel, with consequent agglomeration of the carbon black is avoided.

The invention will be further described with reference to the drawing accompanying the provisional specification which illustrates apparatus especially suitable for carrying out the process according to the present invention. Figure 1 represents a longitudinal section of an apparatus the essential part of which is a horizontal tube capable of being rotated about its longitudinal axis. Figure 2 shows a cross-section of the said tube. Figure 3 represents a vertical section of an apparatus fitted with a vertical decomposition vessel. Figures 1 and 2 have reference to Example 1 and Figure 3 to Example 2, which Examples illustrate how this invention may be carried out in practice, but the invention is not restricted either to these Examples or to the specific kind and arrangement of the apparatus shewn in the accompanying drawing. The parts given in the Examples are by weight, except when otherwise stated.

EXAMPLE 1.

5 grams of fine cobalt powder obtained by the decomposition of cobalt carbonyl are introduced into the horizontal vessel A, shewn in Figure 1. This vessel is 60 centimetres long and 20 centimetres in diameter and is caused to rotate about its longitudinal axis. Its inner wall consists of manganese-copper and is provided with longitudinal ribs B shewn in Figure 2, which ribs also consist of manganese-copper. After hydrogen has been led through the vessel for 3 hours, the vessel being kept at 350° Centigrade by means of the electrical heating jacket C, a gas mixture obtained by the high temperature carbonisation of brown coal and carefully purified from sulphurous impurities (composition: 13.5 per cent. of carbon dioxide, 5.7 per cent. of carbon monoxide, 17.5 per cent. of methane, 3.1 per cent. of ethane, 1.8 per cent. of propane, 28.9 per cent. of ethylene, 12.8 per cent. of propylene, 6.4 per cent. of butylene and 10.3 per cent. of nitrogen) is led through the pipe D into the vessel A with a velocity of flow of 70 litres per hour, the vessel being kept at from about 370° to 380° Centigrade. The mixture of the carbon black thus formed and the catalyst rotates with the vessel through about 120° by reason of the longitudinal ribs B, falls through the free gas space by reason of its weight and is then raised again by subsequent ribs. The gas leaving the vessel through the outlet E contains about 70 per cent. of hydrogen. After about 8 hours the vessel contains 500 grams of an extremely voluminous soft deep brown-black carbon black having an entirely homogeneous nature which is eminently suitable for direct employment as a filler for the production of rubber or rubber-like masses respectively from natural rubber or polymerisation products of butadiene. Part of the carbon black containing catalyst is collected in the vessel F and may be removed at G. The catalyst is separated from the carbon black by dissolution in acids.

EXAMPLE 2.

A vertical decomposition vessel N shewn in Figure 3, 1 metre in length and 15 centimetres in diameter in which is situated a gas-tight rotating axle K provided with sloping surfaces S and funnels M of galvanised sheet iron arranged alternately one above the other in the form of a screen and also provided with galvanised scrapers O, of which only one is shewn in the Figure is heated by means of the electrical heating jacket R so that the internal temperature is from 380° to 400° Centigrade, and 200 litres of carbon monoxide per hour are led in at F. At the same time a finely powdered catalyst consisting of a mixture of about 80 per cent. of cobalt, 10 per cent. of nickel, 7 per cent. of zinc, 2.5 per cent. of calcium oxide and 0.5 per cent. of potassium carbonate, which has been previously subjected to a reducing treatment with hydrogen, is introduced at the top by means of a conveyor worm P. The carbon monoxide is practically completely decomposed into carbon dioxide, which is withdrawn at the outlet J, and carbon black. The carbon black falls into a

vessel arranged at the lower end of the decomposition vessel in the form of a loose powder and may be periodically or continuously withdrawn at H. The catalyst intermixed therewith may be removed by stirring with dilute nitric acid warmed to 50° Centigrade. The resulting carbon black has an extremely high degree of dispersion.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. In the manufacture and production of carbon black by thermal decomposition with catalysts of gaseous or vaporous carbon compounds, causing the catalyst to fall through the gases or vapours to be decomposed, and interrupting the state of fall repeatedly.

2. In the process as claimed in claim 1, employing conveyor worms, bucket wheels, scrapers, shaking sieves or spreaders in the decomposition chamber as the means for causing the catalyst to fall through the reaction space and to interrupt the fall.

3. In the process as claimed in claims 1 and 2, employing the catalyst with a grain size having a mean diameter ranging below 0.1 millimetre and advantageously between 0.01 and 0.0001 millimetre.

4. The process for the production of carbon black substantially as described in each of the foregoing Examples.

5. The process for the production of carbon black substantially as described with reference to the drawing accompanying the provisional specification.

6. Apparatus for the production of carbon black substantially as described with reference to Figures 1 and 2 and in Figure 3 respectively of the drawing accompanying the provisional specification.

7. Carbon black when obtained according to the processes claimed in claims 1 to 5.

Dated this 13th day of March, 1931.

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Fig. 1

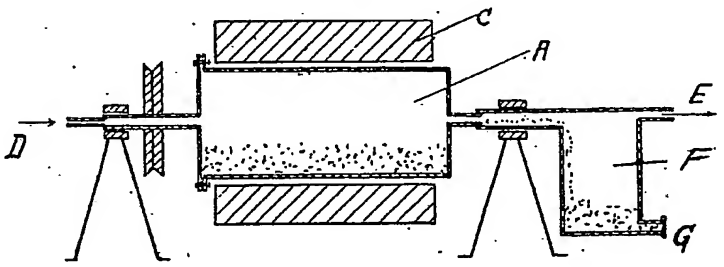



Fig. 2

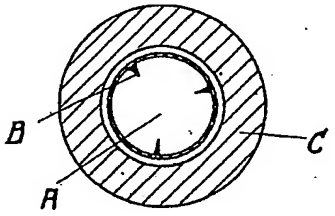
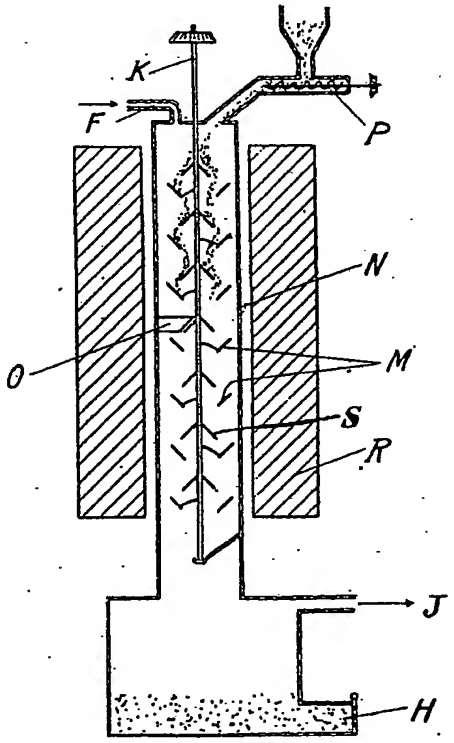



Fig. 3




[This Drawing is a reproduction of the Original on a reduced scale.]

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